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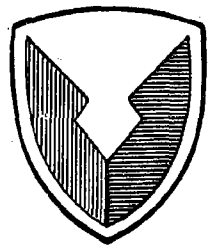

CCL REPORT NO. 153

AN ADAPTATION AND EXTENSION OF A QUANTITATIVE INFRA-RED METHOD FOR THE ESTIMATION OF THE NITROGEN RESIN CONTENT OF MODIFIED ALKYDS

BY

M. L. ADAMS

AMCMS CODE NO. 5025.11.84205
DA PROJECT 1-H-0-24401-A-110-05

10 JANUARY 1964

ABERDEEN PROVING GROUND
MARYLAND

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AUTHOR: M. L. Adams
M. L. ADAMS, Chemist
Chemical Cleaning &
Corrosion Branch

REVIEWED BY: M. Rosenfeld
M. ROSENFELD, Chief
Chemical Cleaning &
Corrosion Branch

APPROVED BY: C. F. Pickett
C. F. PICKETT, Technical Director
U.S. Army Coating & Chemical Laboratory

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ABSTRACT

An adaptation and extension of a previously published infra-red absorbance ratio method for the analysis of vacuum dried films of nitrogen resin modified phthalic alkyd resins is outlined and shows improved accuracy and the inclusion of the determination of benzoguanamine-formaldehyde not previously covered.

I. INTRODUCTION

Federal Specifications TT-E-489c and TT-E-529a for Class B baking alkyd enamels, call for the presence of 10 - 20% of a nitrogen modifying resin. Miller and Shreve (1) developed an infra-red absorbance ratio method for determining urea-formaldehyde and melamine-formaldehyde in such formulations. The results obtained using their method were found to be erratic, particulary for the melamine-formaldehyde content, mainly due to the fact that the 12.25 u band used for estimating its content is proportionally very weak thus leading to absorbance readings well below 0.1.

In the adaptation outlined here, the NH deformation frequency at 6.43 u is used for the measurement of melamine-formaldehyde. Since it has been found that one rather than mixtures of nitrogen resins are present, the accuracy of the method also has been improved by basing the standardizations on two component systems rather than three. The Miller and Shreve method has been extended to include the determination of benzoguanamine-formaldehyde which is now also used as the modifying resin.

II. DETAILS OF THE METHOD

A. Standardization

Known mixtures of a short to medium oil length phthalic alkyd resin and each of the nitrogen resins are prepared in which the nitrogen resin content varies from 10 to 20% by weight on the non-volatile basis. Uniform films of the mixtures are spread on rock salt plates and dried for 15 minutes in a 70°C. vacuum oven.

Using a double beam infra-red recording spectrophotometer with sodium chloride optics, quantitative settings, and a rock salt plate in the reference beam, zero and 100% are set at 5.25 u with the sample in place. The spectrum is then scanned to approximately 7 u. Base lines are drawn as indicated in Figure 1. For each standard the ratio of the absorbance at 5.76 u due to the alkyd portion to that due to the nitorgen resin, 6.09 u for urea-formaldehyde, 6.43 u for melamine-formaldehyde, and 6.45 u for benzoguanamine-formaldehyde, is calculated, the absorbance values being those measured from the point of maximum absorption to the base line. Ideally, the thickness of the film should be such that the alkyd absorbance is no greater than 0.6 and the nitrogen resin no less than 0.1. The absorbance ratios obtained for the standards are then plotted against the ratios of the weight percentages on a nonvolatile basis of alkyd to nitrogen resin.

In this work a Perkin-Elmer model 21 infra-red spectrophotometer was used with settings of: resolution, 960; response, 1; suppression, 0; an up scale signal, and a slow scanning speed. The standard curves shown in Figure 2 were obtained from the data recorded in Table I.

B. Determination of the Nitrogen Resin Content in Unknowns

A thin uniform film of the isolated vehicle is spread on a rock salt plate and carried through the procedure outlined under the standardization. In order to determine the type of nitrogen resin present, after the quantitative scanning from 5.25 to 7 u is completed, the balance of the spectrum to 15 u

is scanned rapidly. As indicated in Figure 1, the presence of urea-formaldehyde is indicated by the absorption band at 6.09 u, melamine-formaldehyde by the band at 12.25 u, and benzoguanamine formaldehyde by the bands at 12.07 u and 12.75 u. The absorbance ratio for alkyd to nitrogen resins is calculated and the concentration ratio, C_R, of alkyd to nitrogen resin determined from the appropriate standard curve.

Calculation

$$\% \text{ nitrogen resin} = \frac{100}{C_R + 1}$$

III. DISCUSSION

Two portions of the infra-red spectra of the three nitrogen resins blended with alkyds are illustrated in Figure 1. Also shown are those bands used for the identification of the nitrogen resin present, the bands used for absorbance measurements, and the positions of the base lines.

Standard curves obtained from the data in Table I are presented in Figure 2.

Table II compares the infra-red results obtained on several qualification samples with those obtained by chemical analysis.

In the Tables and Figures the following abbreviations are used. Absorbance, A and A_R is the ratio of absorbance due to the alkyd to that due to the nitrogen resin; weight percentage concentration, C and C_R is the ratio of percent alkyd to percent nitrogen resin on a nonvolatile basis; alkyd resin, PA; benzoguanamine-formaldehyde, BF; melamine-formaldehyde, MF; urea-formaldehyde, UF.

The infra-red method offers adequate accuracy with a substantial reduction in time of analysis; a sample can be completed in less than half an hour including the drying time. In the event of apparent failures or border line results it may be advisable to apply a chemical determination as a check.

IV. REFERENCES

Miller, C. D. and Shreve, O. D., Anal. Chem. 28, 200-1 (1956).

APPENDIX A

Tables

TABLE I

STANDARDS

I. Alkyd: benzoguanamine-formaldehyde

$A_{5.76}$	$A_{6.45}$	C_{PA}	C_{BF}	A_R	C_R
0.314	0.137	77.2	22.8	2.3	3.4
0.583	0.090	90.8	9.2	6.5	9.9
0.515	0.055	93.7	6.3	9.4	14.9

II. Alkyd: melamine-formaldehyde

$A_{5.76}$	$A_{6.43}$	C_{PA}	C_{MF}	A_R	C_R
0.295	0.086	79.3	20.7	3.4	3.8
0.578	0.112	84.6	15.4	5.15	5.5
0.598	0.055	91.9	8.1	10.9	11.3

III. Alkyd: urea-formaldehyde

$A_{5.76}$	$A_{6.09}$	C_{PA}	C_{UF}	A_R	C_R
0.697	0.180	79.9	20.1	3.9	4.0
0.598	0.111	83.9	16.1	5.4	5.2
0.761	0.102	87.7	12.3	7.5	7.1

TABLE I

ANALYSIS OF SOME COATINGS

Nitrogen Resin Present	A_R	C_R [1]	% Nitrogen Resin by Infra-red [2]	% Nitrogen Resin by Chemical Anal.
BF	3.9	5.9	14	14
BF	4.2	6.4	13.5	13
MF	5.2	5.6	15	15
MF	8.4	8.8	10	10
MF	3.7	4.1	19.5	19
MF	8.1	8.5	10.5	10
UF	5.0	4.8	17	16
UF	7.1	6.6	13	12
UF	9.1	8.3	11	11
UF	7.2	6.7	13	14

1. C_R determined from appropriate standard curve

2. % nitrogen resin $\frac{100}{C_R + 1}$

APPENDIX B

Figures

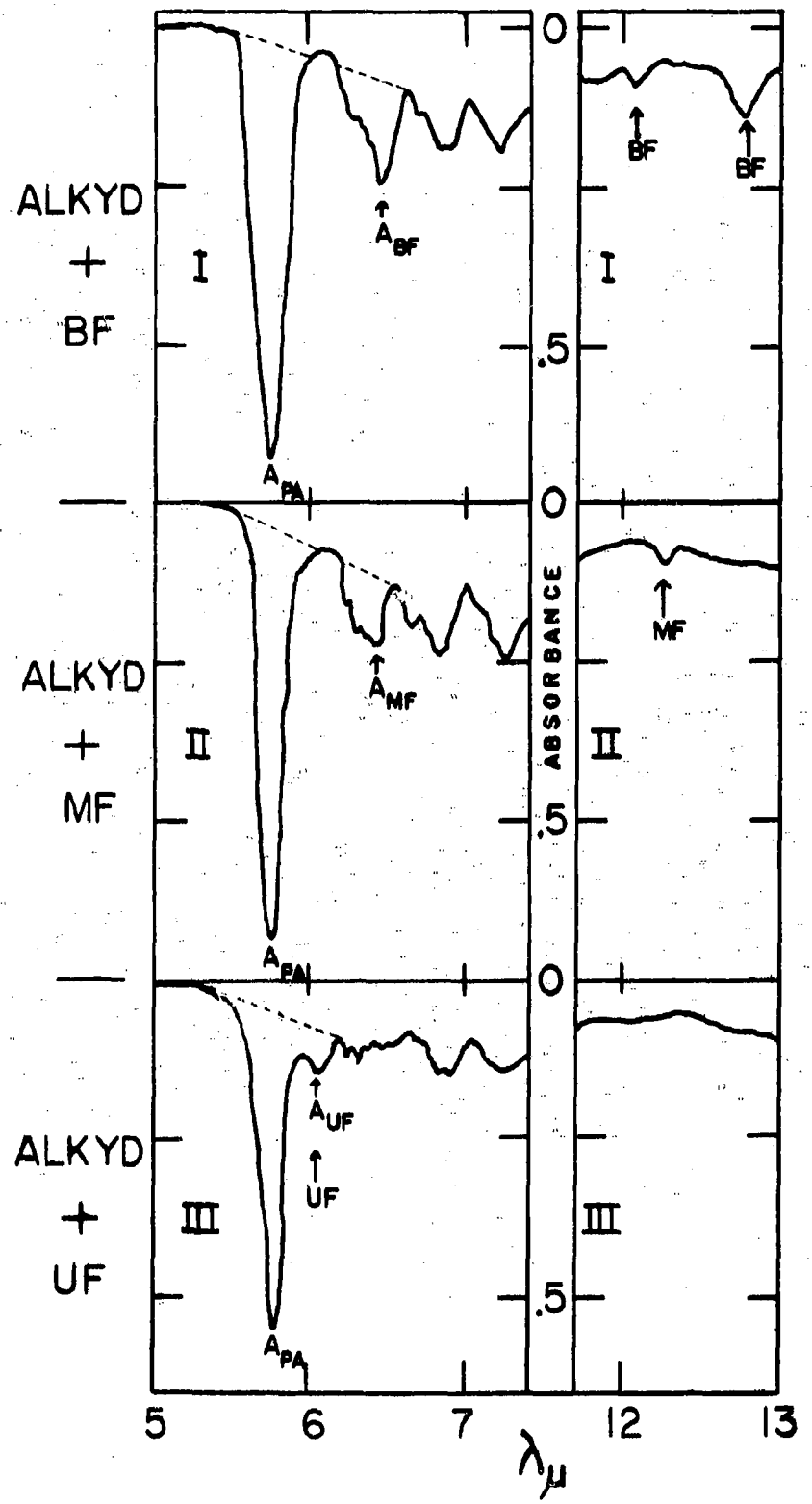
ALKYD
+
BF
I
A_{BF}
A_{PA}
BF
BF
I
ALKYD
+
MF
II
A_{MF}
A_{PA}
MF
II
ALKYD
+
UF
III
A_{UF}
UF
A_{PA}
III
0
.5
0
.5
0
.5
ABSORBANCE
5
6
7
12
13
λ_μ

FIGURE 1

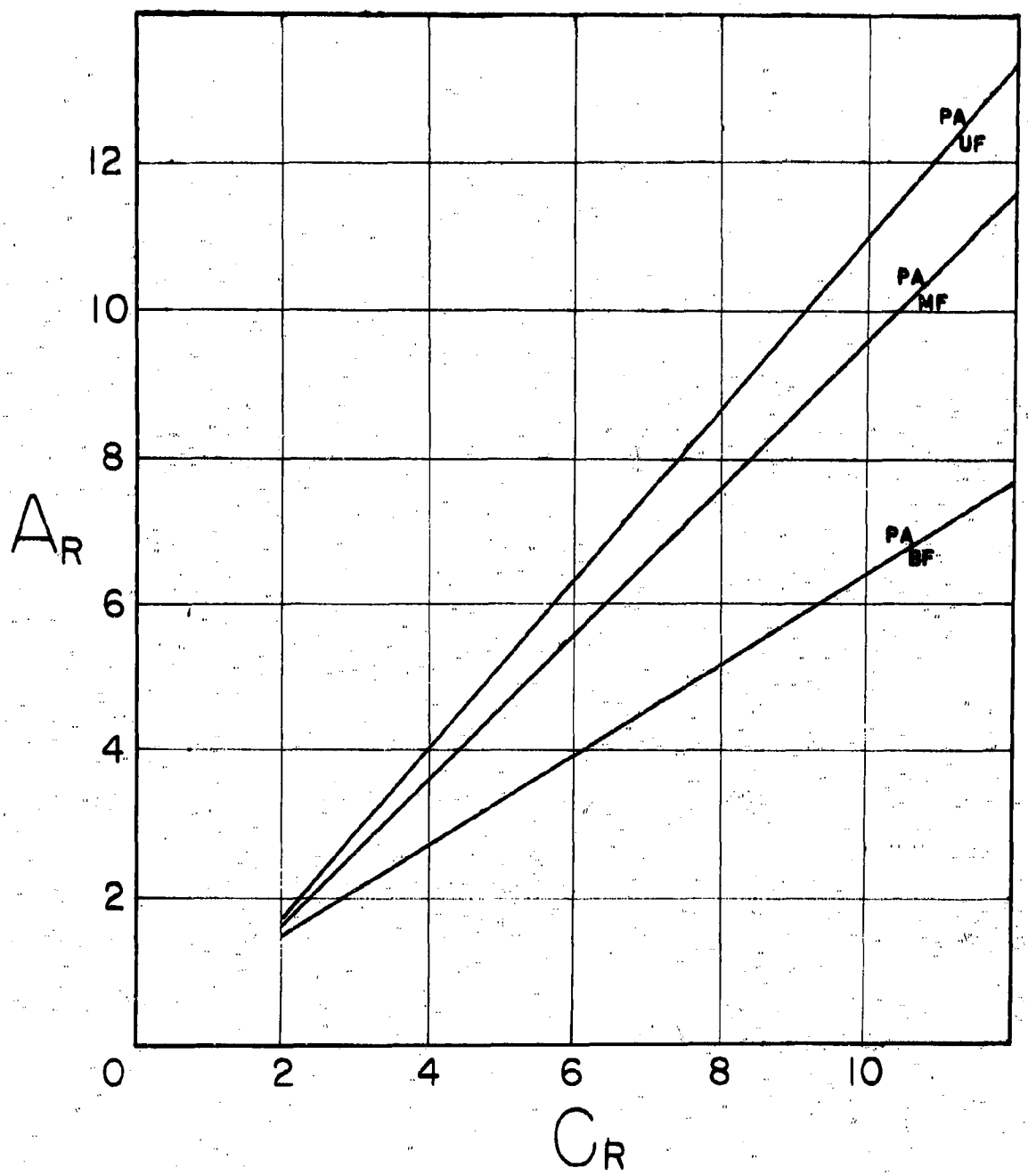

FIGURE 2

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